



A facile route to search antioxidant additives for dry charged negative plate of the lead acid battery

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ABSTRACT

Here we report a new way to characterize the performance of antioxidant additives for dry charged negative plate of the lead acid battery by measuring the anodic excursion peaks (AEPs). Cyclic voltammetry (CV), and linear sweep voltammetry (LSV) combined with potential step method have been conducted to investigate the effects of polyhydric compounds (sorbitol) and cetyltrimethyl ammonium bromide (CTAB) on AEPs and corrosion resistance. The results show that sorbitol increases AEPs but prevents the formation of PbO_2 , and on the contrary CTAB promotes the formation of PbO_2 but eliminates AEPs. These phenomena reveal that the increase of AEPs and the increase of corrosion resistance of lead electrode are synchronous, which indicate that the additives that can enhance AEPs could be used as antioxidant additives. The effectiveness of the new AEPs test on searching antioxidant additives for protection of lead electrode has been compared with the general potentiodynamic polarization (Tafel) method, and the results of the two tests are consistent. Also, it has been obtained that characterizing the antioxidative effect of antioxidant additives on lead electrode via measuring AEPs in CV or LSV is reliable and more facile than Tafel.

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1. Introduction

One way of the formation of plates in lead acid battery is to form the plates before assembling a completed battery. The advantage of this method is that the battery with dry charged plates could work as soon as the electrolyte is added, and does not need initial charge with a long time. But, the cotton-shaped lead on dry charged negative plate is easily oxidized in humid air, which would cause the loss of the capacity. Therefore, in order to reduce the self-discharge of the dry charged negative plate, the surface should be covered with antioxidant additives. So, searching for the effective antioxidant additives for dry charged negative plate is meaningful. The commonly used antioxidant additives include glycerol, glucose, xylitol, etc., and the performance of antioxidant additive is usually characterized by the quantity of corrosion layer monitored over a long period, which is a time-consuming process. The authors of this paper found for the first time that “anodic excursion peaks” (AEPs) of lead in sulfuric acid solution during the voltammetric measurements were significantly increased by the above antioxidant additives.

AEPs are some curious anodic peaks, frequently observed in the cathodic scanning of voltammetric measurements, investigated by

many authors from various aspects [1–10]. It occurs only under the condition when pure lead is polarized with a positive potential, and that just also is the working condition for positive grid of lead acid batteries during charging. Our previous work [11] has exposed that AEPs corresponds to the oxidation of the intermediate PbO_n ($1 < n < 2$), the peak current of which reflects the incomplete oxidation of lead compounds, which means that AEPs may indicate the corrosion resistance of lead electrode. Therefore, the characteristic of AEPs is also critical to the corrosion of the positive grid.

Therefore, in this paper, we try to investigate the effect of additives on the AEPs for the first time, reveal the relationship between the AEPs and the corrosion resistance of lead electrode with additives, and finally to form a new way to characterize the performance of antioxidant additives for dry charged negative plate or positive grid of lead acid batteries.

2. Experimental

2.1. Experimental cell and materials

Sulfuric acid, glycerol, glucose, xylitol, sorbitol, cetyltrimethyl ammonium bromide (CTAB), were reagent grade (from Sinopharm Chemical Reagent limited corporation). Doubly distilled water was used in preparing all solutions. The electrochemical investigations on pure lead were performed in a three electrode system using an

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electrochemical working station (CHI 650C). The $\text{Hg}/\text{Hg}_2\text{SO}_4/4\text{ M H}_2\text{SO}_4$ electrode was employed as reference electrode, and the counter electrode was a platinum foil. The working electrode was a pure lead rod (>99.994%) which was covered with an epoxy resin, exposing an area of about 0.6 cm^2 . Before every experiment, the lead rod was ground successively with abrasive paper, rinsed with anhydrous ethanol (AR) and doubly distilled water. The electrolyte in working cell was 4 M sulfuric acid solution with about 21 mL. And the additive was directly added into the electrolyte solution, which has the amount of about 1% of the weight of the electrolyte solution. All experiments were conducted at ambient temperature ($\sim 25^\circ\text{C}$).

2.2. Voltammetry measurements

According to the literature and our previous results, AEPs occurs when the scanning potential range in CV includes the negative potential at which the PbSO_4 could be reduced to pure lead, and the positive potential where the PbSO_4 could be oxidized to PbO_2 , or when the lead electrode has been successively polarized at the negative potential and positive potential before LSV measurements. So, the scanning potential range in CV was set from -2.2 V to 2.2 V with the scanning rate being kept at 10 mV s^{-1} .

In the second section, LSV measurements combining with potential step polarization were conducted. By this combined technique, the influence of positive polarization on AEPs formation with and without additives and the relationship between the corrosion of lead electrode and AEPs could be investigated effectively. The lead electrode was firstly designed to be prepolarized at -2 V for 60 s, and then polarized at 2 V for different time, enabling the Pb(II) compounds to be oxidized to high-valent lead compounds with different degrees. After polarization, a low-rate LSV measurement was conducted at the potential range from 1.2 V to 0.8 V , where AEPs occurs. And the scanning rate was kept at 5 mV s^{-1} .

2.3. Potentiodynamic polarization measurements

Potentiodynamic polarization (Tafel) measurement is a common method to characterize the corrosion of materials. In order to evaluate the effectiveness of the new AEPs test method and the conventional Tafel measurement on characterizing the

influence of additives on corrosion of the lead electrode, lead electrodes were also investigated via potentiodynamic polarization measurement in electrolyte with and without CTAB or sorbitol in this part. The scanning range was set from -1.3 V to -0.95 V (vs. $\text{Hg}/\text{Hg}_2\text{SO}_4/4\text{ M H}_2\text{SO}_4$), with the scanning rate kept at 1 mV s^{-1} .

2.4. Morphologic analysis of electrode surface

The effects of additives on the surface morphologies of lead electrode when corroded under anodic polarization were examined by SEM with JSM-6380. Before morphologic measurements, three lead rods were prepolarized at -2 V for 60 s and then polarized at 2 V for 100 s in 4 M H_2SO_4 solutions respectively with 1 wt% CTAB, with 1 wt% sorbitol, and with no additives.

3. Results

3.1. CV measurements of AEPs

Considering the antioxidant additives for dry charged negative plate commonly having polyhydric structure, we tried to introduce sorbitol as a new one to investigate its inhibition effect towards the corrosion of lead electrode. Fig. 1 shows the influence of sorbitol and some other antioxidant additives on cyclic voltammograms of pure lead in 4 M sulfuric acid solution, and all curves were identified from the third cycle.

In Fig. 1, peak A corresponds to the oxidation of Pb to PbSO_4 in the anodic scanning process, and represents the generation amount of PbSO_4 under electrochemical polarization, which may be used to characterize the antioxidative effects of additives. But, it was observed that in spite of being antioxidant additives, their effects on peak A varied a lot. Glycerol did not influence peak A, xylitol decreased it, but glucose increased it. The effect of antioxidant additives is to form the protective layer to inhibit the further oxidation, so the oxidation resistance is related to the corrosion resistance of protective layer not the absolute amount of the oxidation of Pb to PbSO_4 under short-term anodic polarization. In this regard, although peak A reflects the quantity of the oxidation of Pb, it is not proper to be used to characterize the antioxidative effect of additives. On the contrary, AEPs was increased by both the three common antioxidant additives and sorbitol in different degrees,

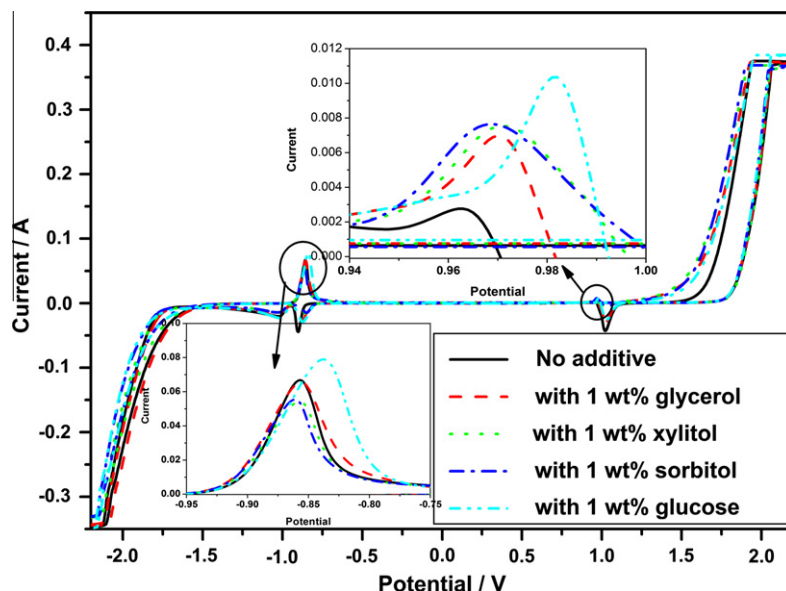


Fig. 1. Voltammograms of lead electrode in 4 M sulfuric acid solution obtained at scanning rate 10 mV s^{-1} , the potential range from -2.2 to 2.2 V , where: (—) with no additive; (---) with 1 wt% glycerol; (····) with 1 wt% xylitol; (- · - ·) with 1 wt% sorbitol; (— — —) with 1 wt% glucose.

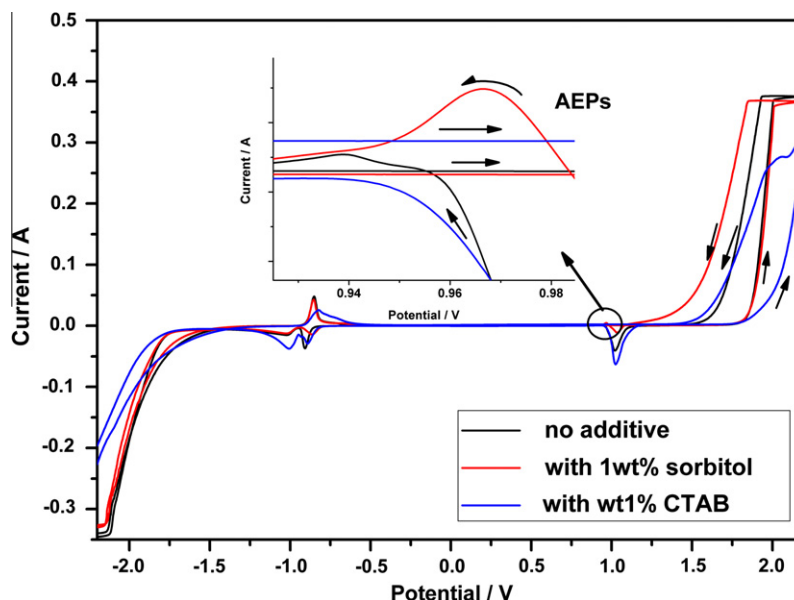


Fig. 2. Voltammograms of lead electrode in 4 M sulfuric acid solution obtained at scanning rate 10 mV s^{-1} , the potential range from -2.2 to 2.2 V , where: (—) with no additive; (—) with 1 wt% sorbitol; (—) with 1 wt% CTAB.

comparing with the blank sample. Therefore, AEPs may reflect the antioxidative effect of antioxidant additives on lead electrode. So, in the following parts, we further investigated the effects of a polyol (sorbitol) and a cationic surfactant (CTAB) on AEPs and on the corrosion of lead electrode, and to find the relationship between AEPs and the oxidation resistance of lead electrode.

From Fig. 2, it has been observed that AEPs was increased about more than two times of the blank sample by adding 1 wt% sorbitol into the electrolyte, whereas AEPs disappeared when the electrolyte contained 1 wt% CTAB. Also, CTAB increased the potential where the anodic current began to rise during the anodic scanning in high potential range, which means that CTAB increases the over-potential for the oxidation of PbSO_4 to PbO_2 and oxygen evolution, but the amount of the formed PbO_2 was increased, reflected by the enhanced peak C for the reduction of PbO_2 to PbSO_4 during the cathodic scanning. It may be ascribed to that even though CTAB makes the oxidation of PbSO_4 to PbO_2 more difficult, the quantity of PbSO_4 involved in the oxidation reaction is also increased, which means that CTAB may increase the amount of the effective reaction centers or increase the specific surface area of the electrode. However, sorbitol moved the potential where the anodic current disappeared significantly lower during the cathodic scanning in high potential range, which means that the oxidation reaction occurs in a large potential range during the cathodic scanning, but the amount of the formed PbO_2 was little, reflected by the mini cathodic peak C for the reduction of PbO_2 . Also the oxygen evolution on the surface of electrode observed during the scanning measurement was not intensive, so the large anodic current may be ascribed to the electro-catalytic oxidation of sorbitol by the formed PbO_2 under high anodic potential [12]. It is concluded that during the process of oxidation of PbSO_4 to PbO_2 , CTAB may promote the formation of the loose structure on surface of lead electrode, accelerate the oxidation of Pb(II) to PbO_2 , and eliminate AEPs, whereas sorbitol inhibited the formation of PbO_2 and at the same time increased AEPs peak currents significantly.

3.2. Potential step and LSV measurements

In order to investigate the influence of the two types of additives on AEPs under different corrosion degree, the lead electrodes

were further measured in this section by combining potential step method and LSV, and the results are shown in Fig. 3. Considering that the oxidation of Pb(II) to PbO_2 is a diffusion-control process, the lead electrode was designed to be polarized at 2 V for different time to achieve the different corrosion degree of lead electrode.

It was observed that peak C for the reduction of PbO_2 increased with the increase of positive polarization time, because the amount of the formed PbO_2 increased with the increase of positive polarization time. When 1 wt% CTAB was in the solution, the cathodic peak C was larger than that obtained in the solution with no additives, whereas when sorbitol was added into the solution, peak C appeared until the positive polarization time reached to 100 s, which means that CTAB promoted the formation of PbO_2 while sorbitol inhibited the oxidation of Pb(II) to PbO_2 . However, the influence of additives on AEPs was on the opposite direction. The sorbitol increased the AEPs, while nearly no AEPs appeared when with CTAB. Also, the occurrence of AEPs needs longer positive polarization time than 10 s when with sorbitol. And when positive polarization time reached to 100 s, AEPs of the blank sample has disappeared, but AEPs of the sample with sorbitol was still high, which means that AEPs still appears even though lead electrode is corroded with a long time in sulfuric acid solution with sorbitol. Via analyzing the trend of AEPs varying with polarization time in Fig. 3, it was obtained that as the polarization time prolonged, the development of AEPs of the sample with sorbitol was later than that of the blank sample. It was obtained that sorbitol inhibited the oxidation of PbSO_4 to PbO_2 , but promote the formation of AEPs. On the contrary, CTAB promoted the corrosion of lead electrode, but eliminated the AEPs. The increase of AEPs and the increase of corrosion resistance are synchronous.

3.3. Tafel polarization measurements

The Tafel polarization curves for lead electrode in 4 M H_2SO_4 in the absence and presence of sorbitol and CTAB were shown in Fig. 4. Also the electrochemical parameters obtained from these curves, free corrosion potential (E_{corr}), corrosion current density (I_{corr}), and the AEPs peak currents obtained from Fig. 3c were compared in Table 1. In order to compare the effect of different additives on AEPs and cathodic peak for PbO_2 reduction, the currents

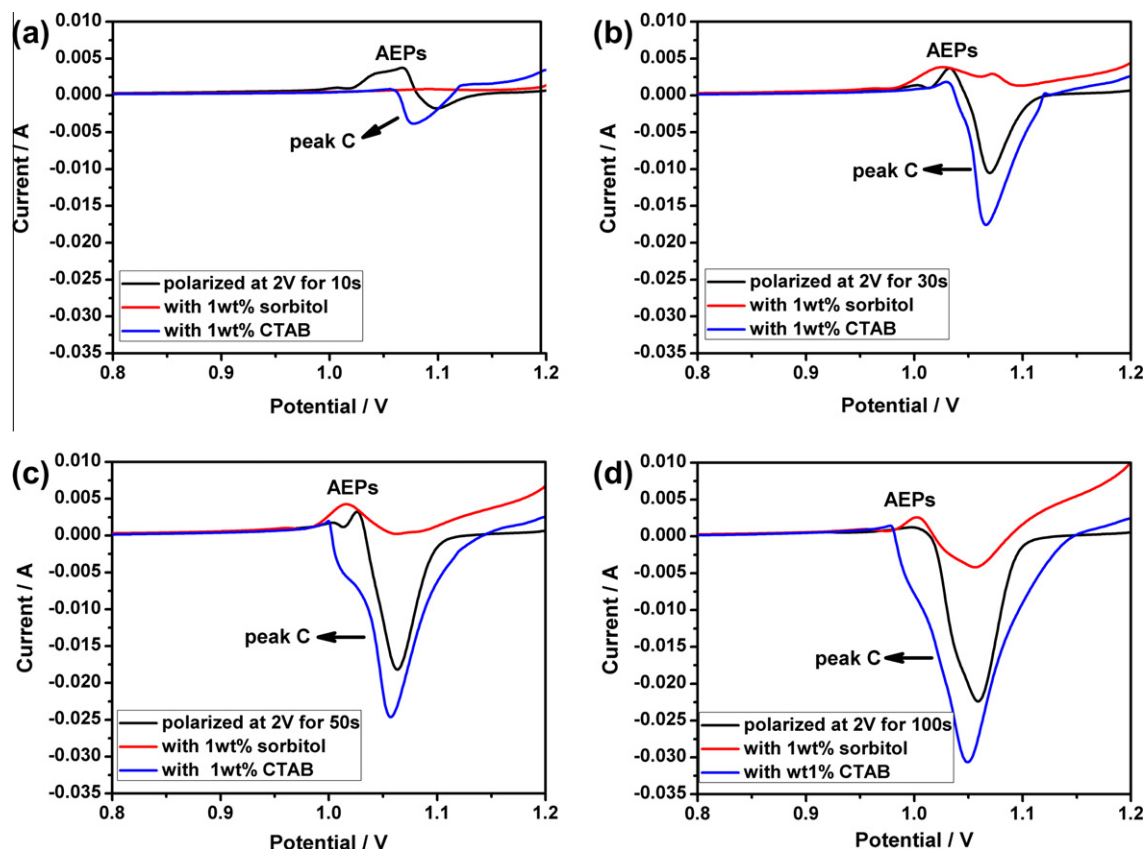


Fig. 3. Voltammograms obtained at 5 mV s^{-1} , the potential range 1.2–0.8 V of samples prepolarized at -2 V for 60 s and stepped to 2 V for 10 s (a); 30 s (b); 50 s (c); 100 s (d), where: (—) with no additive; (—) with 1 wt% sorbitol; (—) with 1 wt% CTAB.

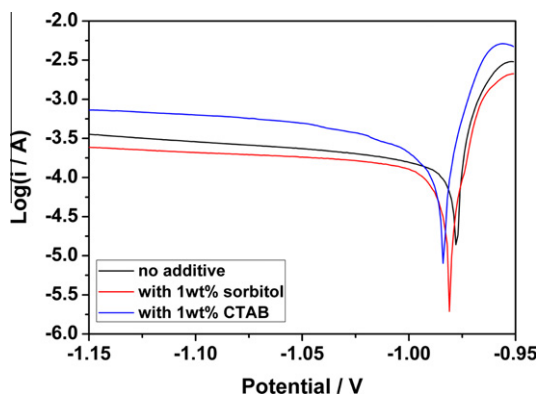


Fig. 4. Tafel polarization curves obtained at 1 mV s^{-1} of samples in $4 \text{ M H}_2\text{SO}_4$, where: (—) with no additive; (—) with 1 wt% sorbitol; (—) with 1 wt% CTAB.

ratio of the anodic excursion peaks and the cathodic peak for PbO_2 reduction obtained from Fig. 3c were also given in Table 1. The results revealed that sorbitol inhibited the corrosion of lead electrode, whereas CTAB promoted the corrosion. The addition of sorbitol decreased the corrosion current density (I_{corr}) and shifted the corrosion potential (E_{corr}) towards positive value. On the contrary, the corrosion current density was significantly enhanced by CTAB, although the corrosion potential had nearly no change. From the data in Table 1, the percentage change of AEPs peak currents with the two additives was the same as that of the corrosion current densities, but the trends just went in the opposite direction, which means that the higher the AEPs peak currents are, the lower the corrosion current densities are. More importantly, the values of AEPs peak currents are high and can be obtained

Table 1

Electrochemical data from Tafel curves and LSV curves carried out in $4 \text{ M H}_2\text{SO}_4$ with and without additives.

Samples	E_{corr} (V)	I_{corr} ($\mu\text{A cm}^{-2}$)	AEPs peak current ($\mu\text{A cm}^{-2}$) Polarized at 2 V for 50 s	The currents ratio of AEPs and peak for PbO_2 reduction
With no additive	−0.978	288	5299.0	0.0175:1
With 1 wt% sorbitol	−0.981	242	6992.2	4195:0
With 1 wt% CTAB	−0.984	737	2770.3	0.67:1

directly from CV or LSV curves, whereas the corrosion current densities are very tiny and require further treatment from Tafel curves. Comparing the currents ratio of the anodic excursion peaks and the cathodic peak for PbO_2 reduction, when sorbitol is added, the ratio is 4195:0 due to the disappearance of the cathodic peak for PbO_2 reduction. In the contrary, CTAB makes the ratio decreased to 67:100. From the point of current ratio, the effect of additive is shown more significantly, which means that the currents ratio of the anodic excursion peaks and the cathodic peak for PbO_2 reduction is higher, the antioxidative effect of antioxidant additives is more. So, we suggested that characterizing the antioxidative effect of antioxidant additives on lead electrode via measuring AEPs in CV or LSV is reliable and facile.

3.4. Effects of additives on surface structure of PbO_2

The effects of the two types of additives on the surface morphologies during the oxidation of PbSO_4 to PbO_2 were examined

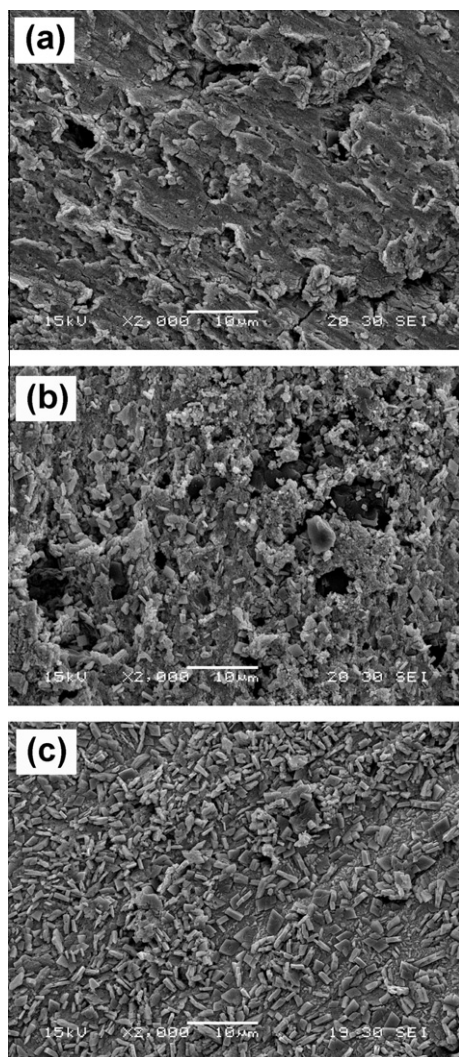


Fig. 5. SEM surface images of PbO₂ prepared by polarizing pure lead rod at 2 V for 100 s in 4 M H₂SO₄ with no additives (a); with 1 wt% CTAB (b); with 1 wt% sorbitol (c).

by SEM. The SEM scanning results were displayed respectively in Fig. 5.

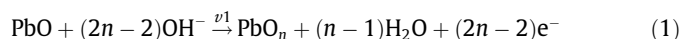
It showed that the sample prepared with no additives has bulk shape with some porous structure at the edge, which is beneficial for the oxidation of the inner layer, which is also the reason why dry charged negative plate is corroded in humid air. When CTAB was added into the electrolyte, the grains have been separated and refining, and the structure has been turned to be loose, which showed that the specific surface area was surely increased by CTAB. The protective layer was destroyed by CTAB and therefore the corrosion of the inner Pb was accelerated. However, sorbitol made the surface covered with small crystal grains, which has compact structure with nearly no pore, and therefore inhibits the corrosion of lead electrode.

4. Discussion

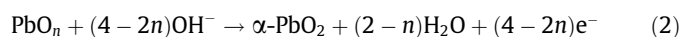
4.1. Relationship between AEPs and corrosion resistance of lead electrode

According to our previous works [11,13], AEPs corresponds to the oxidation of the intermediate PbO_n ($1 < n < 2$) which is the

incomplete oxidation product during the oxidation of Pb(II) to Pb(IV) compounds. After the negative polarization at -2 V, when the potential was stepped to 2 V, the surface of electrode was immediately covered with the Pb/PbO/PbSO₄(O) multilayer structure, where the PbSO₄(O) layer comes from the oxidation of pure Pb, and has a compact structure. The inner PbO was incompletely oxidized to PbO_n at high potential, caused by the low transfer rate of OH[−] species through the outer passivated PbSO₄(O) layer [14]. This process takes place via an electrochemical reaction:



The oxidation degree of PbO depends on the porosity of the outer layer. During the cathodic scanning, the reduction of PbO₂ destroyed the outer compact PbSO₄(O) layer, which benefits the transfer rate of OH[−], and therefore the oxidation of the PbO_n species goes on, which forms the AEPs.

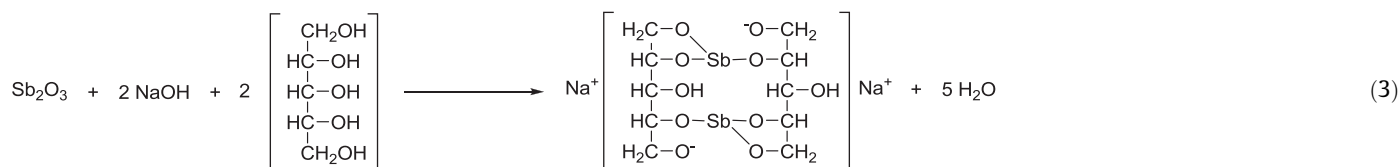


Therefore, the surface structure of lead electrode is the key condition for the formation of AEPs. The more compact the surface of electrode is, the lower the transfer rate of OH[−] is, so the more incomplete of the oxidation of PbO is, and therefore the higher the AEPs is. In this regard, when the electrolyte contains CTAB, the surface of lead electrode was destroyed and became loose (see Fig. 4b), which benefits the ion-transfer, and therefore the inner PbO could be oxidized to α -PbO₂ in a large degree, which means that the quantity of the intermediate PbO_n compounds is small, so AEPs was decreased by CTAB. Therefore, the porous structure benefits the oxidation of lead electrode and the corrosion is accelerated.

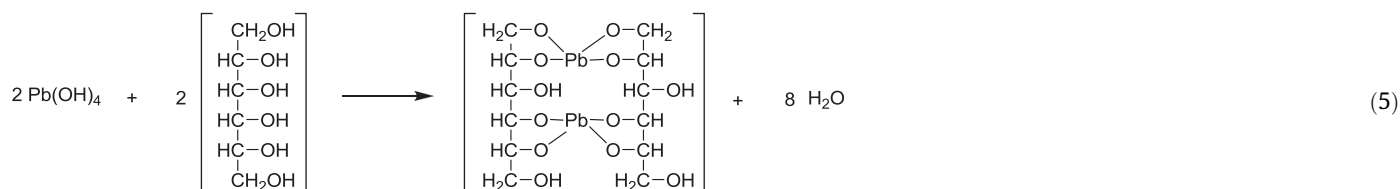
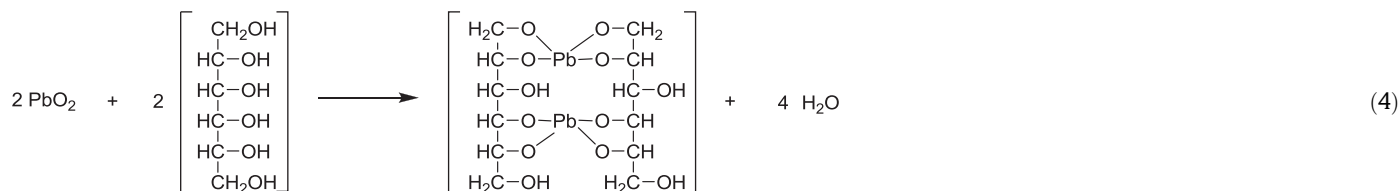
On the contrary, when sulfuric acid solution contains sorbitol, the surface of lead electrode had a compact structure (see Fig. 4c), which inhibits the oxidation of outer PbSO₄(O) to β -PbO₂ and the oxidation of the inner PbO to PbO_n shown in Eq. (1), which caused that nearly no anodic and cathodic peak was observed when the polarization time was 10 s (see Fig. 2a). As the polarization time was extended, the amount of the incomplete oxidation product PbO_n increased, so AEPs increased. Even though the polarization time reached to 100s, AEPs was still high, which means that the protective layer is compact enough to prevent the oxidation of inner PbO even under corrosion with long time. AEPs roots from the incomplete oxidation products in the inner layer, which depends on the outer protective layer. Therefore, the occurrence of AEPs is the character of lead electrode with high corrosion resistance, and also the higher the AEPs is, the higher the corrosion resistance of lead electrode is. So the additives that can increase AEPs of lead electrode in sulfuric acid solution could be used as antioxidant additives on dry charged negative plate of lead acid batteries, which provide a facile way to search antioxidant additives.

4.2. Mechanism of the inhibition of sorbitol

According to the literature, some metallic oxides such as, CuO [15], Sb₂O₃ [16], PbO₂ [17,18] could form coordination compounds with polyhydric alcohols. Grigoriev and Machavariani [19] has investigated the adsorption of fatty alcohol, ethanediamine and glycerol on mercury and lead, and found that the adsorption equilibrium constants of various alcohols on lead are lower than that on mercury, except glycerol with a O-hydroxy structure, which has been ascribed to the coordinated interaction between lead and glycerol. Zhang et al. gave the bonded way between Sb₂O₃ and xylitol as follows:



In the same way, we suggest that PbO_2 and $\text{Pb}(\text{OH})_4$ bond with sorbitol in the following formula:



Pavlov and Monahov[20] suggested that lead electrode has a structure of $\text{Pb}/\text{PbO}_n/\text{PbO}_2/\text{Pb}(\text{OH})_2/\text{H}_2\text{SO}_4$ during the oxygen reaction and on oxidation of Pb and PbO_n . The anodic layer

comprises three sublayers: a PbO_n reaction layer close to the metal, a PbO_2 crystal layer, and a gel layer near the interface with the solution.

According to the above information, we give the model of surface structure of lead electrode covered with sorbitol when polarized at high potential in high degree or when exposed to humid air in Fig. 6, which respectively represents the surface of positive grid during charging or dry charged negative plate of lead acid batteries exposed to humid air covered with sorbitol. Sorbitol molecules attach firmly on the surface gel layer via coordinate bonds, and the remaining hydroxyl groups also attach with other sorbitol molecules through hydrogen bonds, and therefore the surface of lead electrode is covered with a protective layer. Therefore, when lead electrode is polarized at high potential in sulfuric acid solution containing sorbitol for a long time, the surface has a structure of $\text{Pb}/\text{PbO}_n/\text{PbO}_2/\text{sorbitol}$ (in Fig. 6a). Due to the outer sorbitol layer, the transfer of OH^- is prevented, so the inner PbO can not be oxidized thoroughly and large amount of PbO_n emerge. Hence, AEPs increases and the further corrosion is inhibited. In this regard, when lead electrode is polarized in 4 M H_2SO_4 with sorbitol, the oxidation is prevented and the reaction rate is very low, so the formed PbO_2 has small grains, and the surface has compact structure (see Fig. 5c). When the dry charged negative plate of lead acid batteries is exposed to humid air, the gossypine lead is corroded via the following reaction:



If the dry charged negative plate is covered with sorbitol, lead molecules coordinate with sorbitol molecules to form the protective layer, which prevents the transfer of O_2 and H_2O molecules to the inner layer, and hence the corrosion is inhibited.

5. Conclusion

This study was focused on the effects of additives on AEPs formation, and the relationship of the AEPs formation and the corrosion resistance of lead electrode. Through the investigations, the results were obtained as follows:

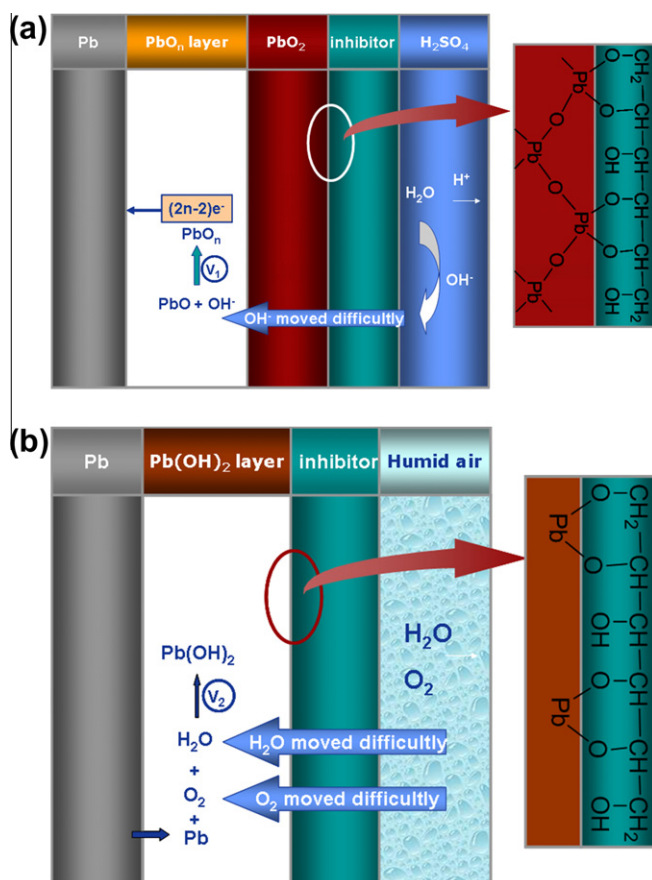


Fig. 6. (a) A model of the structure of lead electrode when polarized at 2 V with a long time in 4 M H_2SO_4 containing sorbitol; (b) a model of the structure of lead electrode covered with sorbitol layer when exposed to humid air.

- (1) From the voltammetry measurements, it was found for the first time that the commonly used antioxidant additives on dry charged negative plate of lead acid batteries and sorbitol increased AEPs of lead electrode in sulfuric acid solution, but CTAB eliminated it. On the contrary, the formation of PbO_2 was prevented by sorbitol but promoted by CTAB. Therefore, the increase of AEPs and inhibition of the oxidation of lead electrode are synchronous.
- (2) The formation of AEPs needs the compact passivated surface, while the compact passivated surface could protect the inner Pb from corrosion. Therefore, the occurrence of AEPs is the character of lead electrode with high corrosion resistance. From this, the effect of additives on inhibition of corrosion of lead electrode could be reflected by AEPs, which provide a facile way to characterize the effect of antioxidant additives. The result of AEPs test on corrosion resistance of lead electrode was consistent with that of general Tafel measurement, and more significantly, AEPs test seems more facile.
- (3) The mechanism of the inhibition of sorbitol on lead corrosion was suggested. Sorbitol molecules are attached firmly on lead electrode via coordinate bonds to form protective layer, which prevent the transfer of OH^- or O_2 into the inner, and hence the corrosion is inhibited.

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